VACUUM SUBLIMATION KINETICS OF UREA NITRATE

B. M. BORHAM* and F. A. OLSON

Department of Metallurgy and Metallurgical Engineering
University of Utah, Salt Lake City, Utah 84112 U.S.A.

(Received October 29, 1979)

Urea nitrate completely sublimes in a continuously pumped vacuum at a rate dependent upon the extent of the surface area. The fraction sublimed ($x$) vs. time ($t$) curve is sigmoidal in shape with an inflection point fluctuating between 5.3 and 8.1% weight loss in the temperature range 56 to 97°C.

The experimental data fit the grain burning model

$$1 - (1 - \beta)^{1/3} = k_s(t - t_0)$$

where $\beta = x$, $\beta = 0$ at inflection point

$\beta = \alpha - \beta_0$, $\beta_0$ and $t_0$ are the respective values of $\alpha$ and $t$ at the inflection point. This equation yielded an activation enthalpy of sublimation of $79 \pm 5.4$ kJ/mole.

Sublimation of urea nitrate was measured using a thermogravimetric method in the temperature range 56 to 97°C under a continuously pumped vacuum. Four rather conclusive evidences support the conclusion that the weight loss was exclusively due to sublimation allowing a kinetic treatment of vacuum sublimation of urea nitrate.

Firstly, 100% weight loss was possible. Secondly, the study was well below the lowest possible decomposition temperature of about 105°C. Thirdly, a 30 mg sample was placed in a 4 mm I.D. by 20 cm long sample tube and evacuated continuously with about one-third of the tube being inserted in boiling water (94°C) and the urea nitrate disappeared from the bottom of the sample cell and condensed on the walls of the upper part of the sample cell which were at room temperature. The sublimate was about 95% of the initial sample weight and on the basis of X-ray and infrared measurements it was found to be urea nitrate. Fourthly, an 8 mg sample was heated at 66°C under continuous vacuum in the thermogravimetric system [1] and the residues after 8% and 69% weight loss were respectively analyzed by infrared spectroscopy. The infrared patterns of both of these residues were the same and matched exactly that of the original urea nitrate showing that no decomposition had occurred.

Experimental

*Technique. A thermogravimetric system utilizing a Cahn R. G. electrobalance with a sensitivity of 0.05 μg was used to monitor the fractional weight loss-time curve. The system was pumped continuously with a mechanical vacuum pump.

* Currently with Anaconda Copper Co., Box 27007, Tucson, AZ, 85726.

J. Thermal Anal. 19, 1980
The temperature was controlled to ±0.1° using a Thermatrol regulator* which was calibrated at the melting point of ice and the boiling point of water. The sample of urea nitrate was synthesized as a powder (10 – 400 μ) by IRECO Chemicals Co., Salt Lake City, Utah. A platinum sample bucket was used during the sublimation study.

**Sample spreading.** It was found that the sublimation rate of urea nitrate was significantly faster with the sample thinly spread in one layer as compared to the compact state. This was explained by the larger surface area exposed to the vacuum for the sample which was thinly spread. Because of this slight dependence of rate on spreading, the results were obtained with a uniform thinly spread sample.

**Sample weight.** The sublimation rate increased as sample weight was decreased but it reached a steady state for samples below 0.42 mg weight at 71°; hence samples less than this weight were used and the sample size was maintained within the limits of 0.22 to 0.29 mg (Table 1). At temperatures less than about 50° it was found that the rate of sublimation of urea nitrate increased continuously as the sample size decreased from 0.368 to 0.184 mg. Hence, data below 50° was not used in the evaluation.

Both sample spreading and sample size effects were quite clearly due to retardation of product gas diffusion effectively creating an over pressure of urea nitrate vapor which then reduced sublimation.

### Results and discussion

**Kinetic study.** The fraction sublimed (α) as a function of time (t) for the temperature range 55.8 – 97° is presented in Fig. 1. The curves show an initial increase of sublimation rate to an inflection point but thereafter show a smooth decrease in rate as a function of time approaching zero residue, or total sublimation, asymptotically. This type of result fits the burning sphere model [2, 3] as given by:

\[ 1 - (1 - \beta)^{1/3} = k_s(t - t_0) \]  

* Halikainen Co., Berkeley, California.

---

*J. Thermal Anal. 19, 1980*